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ADSORPTION PROCESS ONTO AN INNOVATIVE EGGSHELL-DERIVED LOW-COST ADSORBENT IN SIMULATED EFFLUENT AND REAL INDUSTRIAL EFFLUENTS

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ABSTRACT
As the current global trend towards more stringent environmental standards, technical applicability and cost-effectiveness became key factors in the selection of adsorbents for water and wastewater treatment. Adsorption is by far the most versatile and widely used method for the removal of pollutants due to its high removal capacity and ease of operation at large scale. Recently, various low-cost adsorbents derived from agricultural waste, industrial by-products or natural materials, have been intensively investigated. In this respect, the eggshells from egg-breaking operations constitute significant waste disposal problems for the food industry, so the development of value-added by-products from this waste is to be welcomed. The egg processing industry is very competitive, with low profit margins due to global competition and cheap imports. Additionally, the costs associated with the egg shell disposal (mainly on landfill sites) are significant, and expected to continue increasing as landfill taxes increase. The aim of the present was to provide an overview on the adsorption process both on simulated and real effluents onto eggshell-derived adsorbent. This was accomplished by analyzing the uptake potential for selected contaminants. Real wastewater effluents were studied to determine the effectiveness of this low cost adsorbent. Results obtained shown that eggshell can remove several pollutants from different types of aqueous systems, with great efficiency.

Keywords: Eggshell by-products, Low-cost adsorbents, Adsorption, Wastewater treatment

INTRODUCTION

The presence of toxic contaminants in aqueous streams, arising from the discharge of untreated effluents into water bodies, is one of the most important environmental issues in the field of waste management [1,2]. With the rapid increase in population and growth of industrialization all around the world, quality of both surface and ground water is deteriorating day by day. Treatment of industrial wastewater is increasingly necessary with respect to international regulations which mandated the reduction of different compounds in the cleaned water. Various methods are available for the removal of toxic pollutants from water and wastewater including reverse osmosis, ion exchange, precipitation, electro-dialysis, adsorption etc. Among these, adsorption is by far the most versatile and widely used method for the removal of pollutants due to its high removal capacity and ease of operation at large scale [3-7]. Activated carbon has been the most versatile adsorbent for the removal of various compounds from aqueous solutions.

However, high cost of activated carbon restricts its application, prompting an increased research interest into the production of low-cost alternatives to the commonly used activated carbon. Recently, various approaches have been studied for the development of cheaper and effective adsorbents. These low-cost adsorbents include natural materials, biosorbents, and waste materials resulting from industry and agricultural activities. Although many research works have been done recently to find the potential of using various agricultural-derived alternative adsorbents, so far no efforts have been made to obtain an overview of a specific adsorbent derived from poultry by-products – the eggshell waste – in terms of their removal performance, adsorption capacity, and cost effectiveness. Additionally, despite the fact that industrial effluents contain several pollutants simultaneously, little attention has been paid to adsorption of pollutants from mixtures. Considering this, the aim of the present work is to evaluate the adsorption ability of the eggshell low-cost adsorbent on both simulated and real industrial effluents.

State of Art

The porous nature of eggshell makes it an attractive material to be employed as an adsorbent. The eggshell typically consists of ceramic materials which are arranged in a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer. The spongy and mammillary layers form a matrix composed of protein fibers bonded to calcite (calcium carbonate), representing more than 90% of the material. The two layers are also constructed in such a manner that there are numerous circular openings (pores). The utilization of the eggshell and ESM by-products has started over 1970 with the development of several studies aiming at the calcium supplement and other nutrition sources from the albumin, membrane and matrix of the eggshell, which was processed by crushing and milling to obtain fine particles (flours) for animal use. Several researches have been conducted to evaluate the adsorption ability of eggshell as low cost adsorbent, in artificial wastewater with mono or multi components. This studies demonstrated the effectiveness of this adsorbent in the removal of heavy metals [3,11-16], phenolic compounds [17], dyes [10,18-21] and pesticides [22]. Nevertheless, the optimization of variable parameters such adsorbent dose and contact time [16] remains to be investigated. Arunlertaree and colleagues [23] investigated the removal of lead from manufacturing wastewater by adsorption onto eggshell powder. They have conducted several batch studies at unadjusted pH, reaching the reduction of lead concentration to values below quality standards. Later on, Park and collaborators [24] studied the adsorption of chromium, cadmium and lead from a real electroplating wastewater treatment facility. They identified calcined eggshell as a good adsorbent for treatment of acidic wastewater with a considerable uptake of heavy metals, as result of eggshell neutralization capacity. In the present paper we assess the adsorption capacity of eggshell powder to remove organic and inorganic compounds from both simulated wastewater and different types of real wastewater effluents, comparing the adsorption capacity of eggshell in different operating conditions.

MATERIALS AND METHODS

Adsorption measurement

The adsorption capacity was calculated by determining the final concentration at equilibrium, according to Eq, 1

$$qe = ((C_0 - Ce)*V)/m \qquad (1)$$

where qe (mg/g) is the solute adsorption capacity per gram of eggshell, C_0 and Ce (mg/L) are the concentration at initial and equilibrium, respectively, V (L) is the volume and m (g) is the mass of eggshell used.

Sorbent

The sorbent used in the present paper was eggshell powder, collected from a local hatchery waste. Shells were washed with distilled water and the membrane was recovered by hand. They were left in distilled water overnight. After complete removal of the organic fraction, shell was washed again. Afterwards, the material were dried at 105ºC for 24h, milled and calcined at 1000ºC for 2h.

Concentration of pollutants

The concentration of organic matter was determinate by measuring chemical oxygen demand (COD), by closed reflux method. The concentration of aluminum (Al) and copper (Cu) was given by atomic adsorption spectrometry (AAS), whereas aluminium was measured by nitrous oxide – acetylene and, copper and sodium were determining by Air-acetylene flame method [25].

Preparation of simulated solutions

The copper solution was prepared from stock solution of $CuSO_4.5H_2O$ (Merck) by dissolution in distilled water. The blue methylene solutions were performed from powder blue methylene (C.I. 52015, Merck), by dissolution in distilled water.The chloride solutions were prepared from stock sodium chloride solution, NaCl, by dissolution in distilled water.HCl (0.1N), H2SO4 (0.1N) and NaOH (0.1N) solutions were used to adjust pH values.

Real wastewater system

Three different types of wastewater effluents were analyzed. Removal of organic matter was assessed in municipal wastewater from unit treatment facilities and from landfill leachates, collected from a local landfill plant. Adsorption of aluminium was studied in the wastewater effluent from an aluminium anodizing plant. The samples were recovered in proper containers and stored at 4ºC [25].

Wastewater effluents composition

Table I. Characterization of diferent types of wastewater used in the present paper.

	Municipal	Leachate	Anodizing
pH	7.75	8.38	13.04
CQO [mg/L]	579	5760	
Metals			

Al [mg/L]	870

Experimental batch procedures

To determine the optimized operating conditions for pollutants removal of the different wastewater samples, batch studies were carried out with eggshell powder in a 100 mL beaker of aqueous solution, with agitation and pH control. All batch adsorption studies were conducted at room temperature. To determine the effect of eggshell dosage on the copper and chloride removal, 1, 3, 5 or 8 g/L of eggshell powder were added to each set of experiments. To evaluate copper uptake, the initial concentration was 60 mg/L and for the chloride removal 300 mg/L was used. For the adsorption studies of methylene blue, at initial concentration of 5 mg/L, a range of concentrations varying from 10 to 80 g/L of eggshell powder was used. To determine the removal of organic matter from real wastewater effluents, dosages of eggshell in the range of 5 to 20 g/L were used. For~~t~~ the removal of aluminium, eggshell powder concentrations varied from 1 to 8 g/L.

RESULTS AND DISCUSSION

Adsorption studies at simulated aqueous system

The adsorption capacity of eggshell, for copper and chloride removal, as function of the adsorbent dosage, is shown in Figure 1. It can be stated that the adsorption capacity of eggshell is proportional to eggshell concentration and the best adsorption capacity corresponding at eggshell amount of 1g/L, both for copper and chloride. It is clear that eggshell possesses more affinity to copper than chloride, revealed by the higher value of adsorption capacity found for copper. However, for the higher concentrations of eggshell powder, the removal of both copper and chloride is comparable.

Accordingly, similar results correlating the adsorption capacity with eggshell concentration were obtained by Ghazy and colleagues [12], who demonstrated that Cr (III) uptake decreases with the increasing eggshell concentration.

Figure 2 presents the adsorption capacity of eggshell to remove methylene blue as function of adsorbent amount. The best results obtained for the methylene blue removal were found at an eggshell concentration of 10 g/L. Nevertheless, it worth to be noted that the adsorption capacity is considerable lower than the one obtained for copper and chloride. This could be explained as the eggshell membrane is constructed of a fibrous network of proteins with positively charged surface produced by the basic side chains of the amino acids arginine and lysine. It is not, thus, unreasonable to attribute the adsorption of the dye to electrostatic attraction of oppositely charged species. Considering that methylene blue is a basic dye, this fact would explain its poor adsorption by the eggshell powder [10].

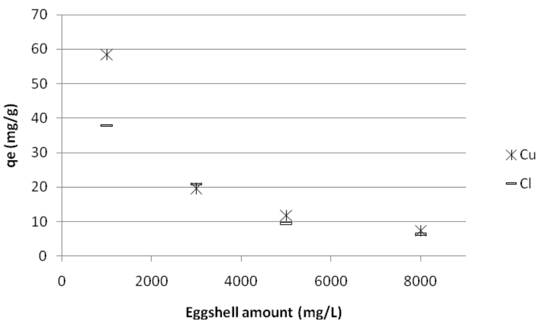

Figure 1. Eggshell adsorption capacity to remove copper (Cu) and chloride (Cl) as a function of adsorbent amount, at inicial concentration of Cu of 60mg/L and Cl of 300 mg/L, both at pH 6.

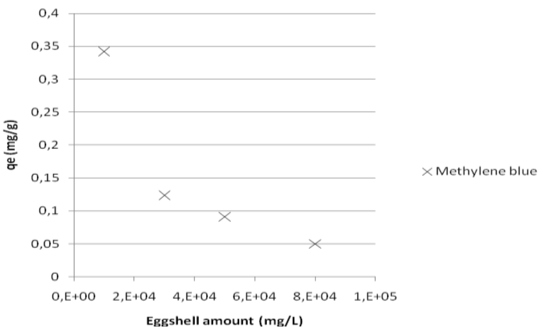

Figure 2. Eggshell adsorption capacity to methylene blue as a function of adsorbent amount, at inicial concentration of methylene blue of 5 mg/L at pH 8.

Adsorption studies at real aqueous system

The adsorption capacity for organic matter, measured as COD (mg/L) versus eggshell concentration is shown in Figure 3. The studies were performed at different pH values considering the importance of this parameter in adsorption process. It is demonstrated that at pH 5, COD removal is higher than the one obtained at unadjusted pH. It was also found that the higher COD adsorption was obtained at 150 mg/L of eggshell powder (not published). For these concentrations of eggshell, the adsorption capacity appears to be similar and independent of the pH adjust. In an industrial process, pH adjustment involves the addition of chemicals thereby increasing the costs of the process and also implying additional treatment of the final solution [23]. For this reason, the studies of COD removal from unit treatment facilities were carried out at unadjusted pH. Figure 3 reveals that adsorption capacity of eggshell is higher for low range COD than for higher ones.

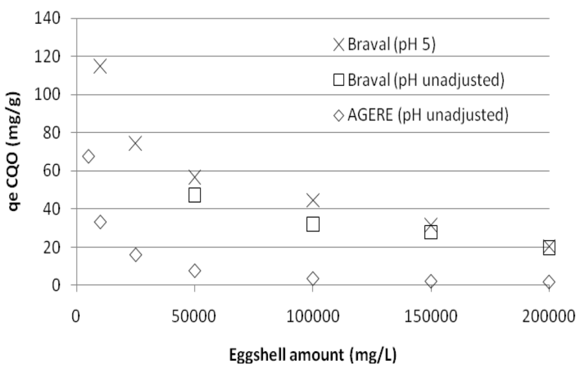

Figure 3. Eggshell adsorption capacity to remove organic matter, measure as CQO (mg/L), as a function of adsorbent amount, at initial concentration of CQO 5760 mg/L for municipal wastewaterl and CQO 579 mg/L for the landfill leachate.

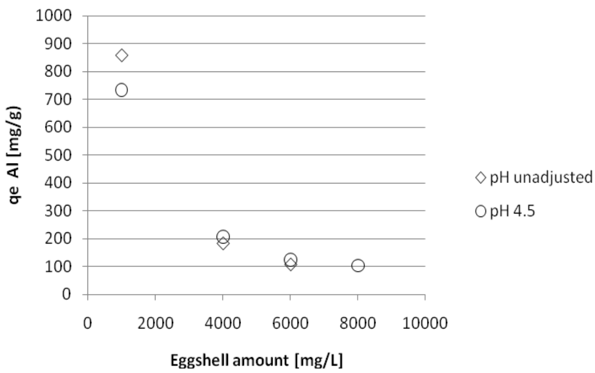

Figure 4. Eggshell adsorption capacity to remove aluminum (mg/L) as a function of adsorbent amount, at inicial concentration of Al 870 mg/L.

Figure 4 shows the adsorption capacity for aluminium from electroplating wastewater effluent, as a function of eggshell concentration, for different values of pH. The pH 4.5 is justified by the speciation curve of aluminum, according to figure 5. At this value of pH, aluminium is found in soluble form, allowing its removal through adsorption. The best adsorption capacity is obtained at unadjusted pH with 1 g/L of eggshell. It appears that for higher concentrations of eggshell, a suddenly decrease of adsorption capacity is found. For 1 g/L of eggshell, is a small there's a slight difference between adsorption at unadjusted pH and pH 4.5.

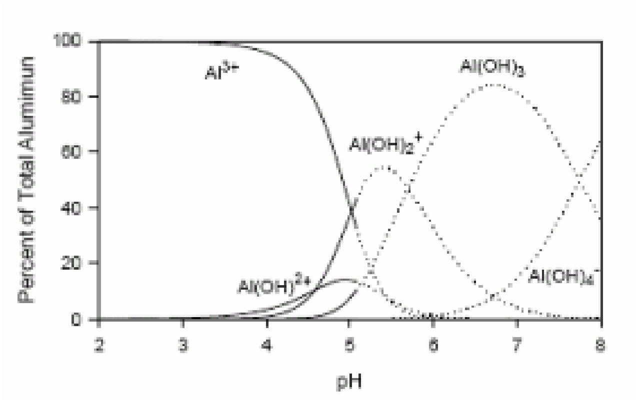

Figure 5. The speciation curve for aluminum [26].

CONCLUSIONS

The results showed that eggshell by-product may be a promising adsorbent for several types of pollutants present in wastewater effluents. For the adsorption of copper and chloride, it was demonstrated that a maximum adsorption capacity was reached when using 1 g/L of eggshell powder. It was also observed that the eggshell adsorbent has a better affinity for copper than for chloride. Regarding the adsorption of methylene blue, the results showed a smaller affinity. The studies involving real wastewater effluents, illustrated the potential of eggshell as a substitute of traditional adsorbents. Concerning the removal of organic matter, from two specific effluents, with higher and low charge of organic matter, results demonstrated a good adsorption capacity for the two cases, without requiring a change on the operating conditions. Additionally, the results obtained for the adsorption of aluminium, prove that eggshell works as an effective adsorbent in wastewater from anodizing plants. From the evidences of all the performed experiments, it is possible to conclude that calcined eggshell is a promising adsorbent for the removal of some types of water pollutants.

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